We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Investigation of the Effective Reinforcement Modulus of Carbon Nanotubes in an Epoxy Matrix

Alfonso Martone, Gabriella Faiella, Mauro Zarrelli,
Vincenza Antonucci and Michele Giordano
*IMCB-CNR Institute for Composite and
Biomedical Materials - National Research Council
Italy*

1. Introduction

Polymer nano-composite matrix could be the ideal solution for a new generation of composite materials. The continuous demand for new high performance polymer composite for various applications, in different industrial sectors, has lead many researchers to investigate the potential use of the carbon nanotubes (CNTs) as nano-reinforcements of polymer matrix for the manufacturing of traditional laminate composite.

CNTs have attracted considerable attention due to their unique mechanical, surface, multi-functional properties and strong interactions with the hosting matrix mainly associated to their nano-scale features. CNTs' impressive mechanical properties, with stiffness and strength values falling within the range of 100-1000 GPa and 2.5-3.5 GPa, respectively, make them ideal candidates to develop novel composites characterized by advanced polymer matrices (Treacy, 1996).

Despite the enormous amount of experimental data available in literature (Coleman et al. 2006, Thosterston et al., 2003), there are still controversial results concerning elastic property, strength and fracture toughness; moreover, due to inherent difficulties in processing these unconventional nanostructure as nano-fillers in polymer system, a reliable theoretical correlation of the experimental data is still in shadow. Different approaches to build an appropriate theory for predicting reinforcement efficiency of CNTs within an hosting matrix have been presented in the literature. Indeed, the reinforcement capability of carbon nanotubes in a polymeric matrix will depend on their amount, but, undoubtedly, their arrangement within the hosting medium plays a fundamental role in the load transfer mechanism. For this reason, the state and level of dispersion need to be accounted in any attempt for predicting the mechanical behaviour of the final nano-composite system.

In literature the enhancing reinforcement of CNT loading for the Young's modulus is commonly reported. However, at the same time, discrepancy among the different data is highlighted. Therefore, an important issue for modelling purpose is the lack of a reliable database for this property.

Characterization and structure-properties of nano-mechanics modelling research have shown that enhancement in mechanical properties of nano-composites are strongly

dependent upon the level of dispersion and the final morphology of the nano-fillers. CNTs dispersion process still represents a critical issue to allow the potential usage of these nano-structure as reinforcements. Dispersion and homogenization stands as a very complex phenomenon due to the natural tendency of CNTs to bundle and to aggregate mainly due to Van der Walls interactions among nanotubes (Martone et al. 2010).

In literature (Martone et al. 2010), various techniques are reported about dispersion of nanotubes in polymer resins. However, despite the enormous number of published works, most of these methods are either limited in capacity or not powerful enough to separate the agglomerates into individual nanotubes. The interested reader can refer to update survey published by Hussein et al. A good dispersion and, possibly, the alignment of CNTs within a matrix represent still a challenge and they could operate as main factors to drive the diffusion of carbon nanotubes as nano-reinforcements on industrial scale. Although these exiting opportunities, till doubts arise concerning the more efficient procedure for the uniform dispersion of the nanotube within polymer system. Thus, experimental data on mechanical property of the final nano-composite appear not always reliable and useful.

A further issue related with the current state of the art within the area of CNT/polymer nano-composite is certainly represented by the achieved level of reinforcement, with single (SWCNT) or multiwalled carbon nanotubes (MWCNT) as fillers in hosting matrix.

From the theoretical point of view, different parameters could be considered to quantify the reinforcement effect of nano-filler within the final nano-composite system. Based on classical Cox's approach, developed for paper and other fibrous materials to analyse the effect of orientation of the fibres on the stiffness and strength, a suitable expression for the effective reinforcement modulus of paper and fibrous materials can be defined as follows:

$$E_{\eta} = \frac{(E_c - E_m)}{V_{filler}} + E_m \quad (1)$$

where E_c and E_m represent, respectively, the modulus for the final composite and the hosting matrix and V_{filler} is the nanotubes volume fraction. Eq. 1 represents the equivalent modulus of reinforcement according to the measured value of the final nano-composite. An expression for the reinforcement efficiency can be properly derived by the eq.1, considering the ratio between the effective reinforcement modulus and the nominal modulus of the reinforcement, as follows:

$$\eta_{ref} = \frac{E_{\eta}}{E_{filler}} = \frac{1}{E_{filler}} \frac{(E_c - E_m)}{V_{filler}} + \frac{E_m}{E_{filler}} \quad (2)$$

where E_{filler} represents the nominal modulus of the loaded filler.

Figure 1 reports the reinforcement efficiency, computed on literature data, taken from different research works.

The data reported, in fig.1, are related with lowest nanotubes content (dilute regime) which should correspond to the minimum level of nanotubes clustering and thus highest level of dispersion for each set of data. Since the nanotubes modulus values range from 1000 GPa to 3000 GPa according to Treacy, the enhancement of elastic modulus showed by the reported data appears extremely low with a remarkable spread.

Analysis of the data reported in fig.1 reveals that the obtained efficiency of reinforcement is sensibly lower than expected, supporting great efforts to develop more standardised manufacturing processes and, hence, to gather more reliable data.

Fig. 1. Reinforcement efficiency, E_η , as function of CNT average aspect ratio for literature data.

This chapter is divided into three main sections. In the first part, the available experimental data concerning the effect on mechanical behaviour of CNTs as nano-fillers will be presented and analyzed; in the second part, a survey of modelling attempts for this property will be presented in order to highlight the major features of reinforcement mechanisms due to CNTs. The last part of the chapter will present a further development of a simple rule-of-mixture based model which accounts for different fundamental features such as contacts and waviness of nano-reinforcing elements within a polymeric system.

2. State of the art on CNTs reinforcement effects

2.1 Experimental evidences

Toward the establishment of carbon nanotubes (CNTs) as prospective mechanical reinforcement of polymers, two fundamental issues need to be addressed: the bulk mechanical properties of carbon nanotube nano-composites as function of nano-filler properties (geometry and shape, i.e. aspect ratio and curliness) and, in addition, the effect of topological distribution of nanotubes within the hosting matrix. Currently, only the first issue has been investigated thoroughly by using different experimental techniques and theoretical models, whilst the morphology of such nano-composites have been extensively studied only by means of electrical and thermal conductivity tests. Enhancing effect of carbon nanotubes in hosting polymer still remains under shadow for two main reasons: the unavailability of reliable experimental data and the unveiling mechanisms of reinforcement associated with nanotubes. In this paragraph, the first section will review the experimental data regarding the mechanical behaviour of CNT-polymer nano-composite, currently available in the literature;

finally, in the second part, the main developed models to predict the enhancement effect will be presented and described.

2.2 Mechanical behaviour of nano-composites

Given the potential of the CNTs as reinforcement agents, several researchers have tenaciously pursued their use in polymer nano-composites, either thermoplastics or thermosetting based system. Despite the huge quantity of available experimental data, it is widely recognised that the results are still controversial.

A paramount issue within the area of nano-composite research and development is represented by the dispersion of the filler within the matrix. In fact, the level of dispersion, in terms of uniformity and disentanglement, influences not only directly, the arrangement of tubes and, hence, the final morphology of the nano-composite, but also, indirectly, their maximum content and their reinforcement mechanism features.

Early investigation on the mechanical behaviour of CNT composites have reported enhancements in Young modulus lower than expected, revealing also negligible increasing or in some cases, significant decrease in strength and toughness.

Ogawasara et al. 2004, have manufactured composites with nanotube content up to 14% in weight, experiencing a quasi-linear behaviour of elastic modulus (see figure 2). In this case, the effective reinforcement of the nanotubes, according to the Coleman parameter (eq.1) results very low (about $E_{\eta}=13$ GPa) and constant as nanotube content increases. Moreover, beyond a certain weight fraction, a significant reduction (-20%) of strength respect to the neat polymer was measured likely due to the inherent difficulties to uniformly disperse the high amount of nano-filler within the hosting matrix.

An early work on mechanical behaviour of polymer loaded with nanotubes was published by Shaffler and Windle in 1999, considering multi-walled carbon nanotubes in PVA system. The reported amount of nano-filler, used in this work, appears incredible high (up to 60%) whereas the gaining in mechanical modulus, measured by dynamic mechanical analyser (DMA), results extremely low ($\eta_E=4.7$ GPa). A complete review up to 2006 for the nominal reinforcement efficiency on Young modulus for various hosting systems, different carbon nanotubes types and dispersive technique is reported in Coleman 2006.

While scientists have studied the CNT induced reinforcement focusing on systems characterised by an “enormous” nano-filler content, other researchers have pointed out the importance of the percolative behaviour of carbon nanotubes (Kovacs et al. 2007, 2009) and have particularly analysed the enhancement contribution of electrical property. It is well know, in fact, that onset transition between insulator conductor behaviour falls at CNT content around 0.10%w, according to both nanotubes aspect ratio and final morphology.

Studies on low volume fraction nano-composites have highlighted an higher mechanical efficiency associated to carbon nanotubes. De Zhang et al., 2004 reported a modulus variation from 0.396 GPa to 0.852 GPa by using only 1 %wt of MWCNTs in Polyamide 6 corresponding to a reinforcement of 91 GPa. They also observed a significant increase in yield strength from 18 to 40 MPa. These results were mainly associated to the achieved good level of dispersion as revealed by the performed microscopy analysis and the reinforcement efficiency was varying according to the CNT content.

Liu et al, 2004 studied the mechanical performances of high aspect ratio nanotubes in a thermoplastic matrix at low volume fraction (<1%). The experimental data of bending modulus and yield strength, presented in this work, showed that the incorporation of a small amount of MWNTs into a polymer matrix can significantly improve those mechanical

Fig. 2. Young Modulus (YM) and Tensile Strenght (TS) data vs nanotube content. Ogasawara et al., 2004;

properties (see figure 3). Microscopy observations indicated the successful achievement of a uniform and fine dispersion of MWNTs throughout PA6 matrix and a strong interfacial adhesion between nanotubes and the matrix, which are responsible for the remarkable enhancements in overall mechanical properties.

Fig. 3. Young Modulus (YM) and Tensile Strenght (TS) data vs nanotube content. Liu et al., 2004;

Data published by Ayatollahi et al. 2011 report a direct proportionality of both Young's modulus and tensile strength for a epoxy polymer filled with different nanotube contents (see figure 4). A limited reinforcement efficiency for the Young modulus and slight increase of the tensile strengths is noticeable.

Very recent data published by Martone et al. (2010) and Martone et al. (2011) revealed that the Young modulus of carbon nanotubes within an hosting polymer system strongly depend upon nano-filler aspect ratio which also affects the critical nanotube content corresponding to a fully connected path (see figures 5). The averaged aspect ratios of the nano-fillers were, respectively, equal to 29 and 55 and 505. It has been verified that, for all cases, the traditional rule of mixture cannot predict correctly the experimental values. In fact, a highly non linear and non monotonic trend, as function of the MWCNT content, was found and a maximum value was observed for each nano-composites modulus curve.

Fig. 4. Young Modulus (YM) and Tensile Strength (TS) data vs nanotube content. Ayatollahi et al. 2011.

The effective reinforcement modulus, E_{η} , results a monotonic decreasing function of the volume nanotubes content for each considered aspect ratios. CNTs contribute to the composite mechanical stiffness with an effective modulus that decreases with arising of the aspect ratio values in the low concentration region and it continuously decreases as the filler content increases. It can be noticed that while the curves trend is independent on the CNT aspect ratio, the CNT reinforcement in very dilute regime ($V_{NT} \rightarrow 0$) is severely a function of nanotube aspect ratio. It worth to note also that the transition region do not overlay with the experimental percolation threshold leading to the conclusion that the progressive development of the nanotubes network within the matrix do affect the mechanical efficiency of the filler even below the formation of the percolative path.

It is worth to highlight the non-linear behaviour of Young's modulus as function of CNT content reported by the curves in fig.5. In fact, the relative enhancement in composite modulus decreases progressively with filler fraction according to Ogasawara, Liu and Ayatollahi, in turn the tensile strength increases linearly with the nanotube content for Ogasawara and Liu, while decreases for higher filler percentage in case of Ayatollahi.

Fig. 5. Young Modulus (YM) data vs. CNT content from a) Martone et al. (2010) and b) Martone et al. (2011)

Figure 6 shows data sets published among the 2004 and the 2011 for the Young’s modulus of CNT-polymer nano-composite at different CNT contents revealing a controversial dependency and very different trends. The reported data sets have been grouped in three distinct categories, according to their functionality with CNT content: inversely linear behaviour in blue colour , non linear behaviour in red colour and almost constant curves in purple.

A linear trend of curve can be recognised for some of these data sets (*blue sets*) whereas some other sets highlight a non-linear functionality with CNT content showing a enhancement of the modulus at certain percentage (*red sets*). In some other cases a negligible proportionality with CNT content (*purple sets*) is recorded conversely with previous data.

Fig. 6. Available literature data of reinforcement efficiency, E_η , vs. CNT content.

Further contradictory findings on experimental data relative to mode I fracture toughness (K_{IC}) are reported in literature, thus driving the actual effort of many researchers to attain better and more reliable experimental information on effective mechanism of reinforcement and enhancement. The geometrical features of carbon nanotubes and processing techniques strongly affect the final results as also confirmed by limited amount of fracture toughness data.

Fig. 7. Fracture toughness of CNTs composites. a) Thostenson and Chou, 2006. b) Zhou et al. 2008.

Thostenson and Chou, 2006 used the calendering technique to disperse MWCNTs in epoxy and used single-edge notch bend (SENB) specimen to measure K_{Ic} . In this work, nano-composites at different loading contents were manufactured by tuning the dispersion parameters (distance between calendar cylinders, temperature, cylinder rates etc...). Both the investigated nano-composites exhibits a maximum enhancement in fracture toughness at low CNTs content (comparable with statistical percolation threshold), followed by a decreasing behaviour (figure 7). The measured maximum K_{Ic} was obtained for 0.2 wt.% of MWCNTs when the gap between the rolls of calendering machine was 10 μ m.

Zhou et al., 2008 investigated the fracture toughness behaviour at low weight content of CNTs recording similar enhancements (figure 7). In this latter case CNTs were dispersed in the matrix by ultra-sonication technique.

Experimental data suggest that CNTs would be able to exploit their potential as structural reinforcement when are nearly isolated in the hosting medium. This latter condition requires not only to manufacture the nano-composites at low CNT volume content, but also to employ high energy dispersion techniques capable to de-bundle the pristine nanotube ropes and aggregates.

A potential approach to enhance the load transfer mechanism matrix could be attained by strengthening the interfacial bonding among nanotubes and hosting system. The functionalization of CNT-surfaces by tailored chemical groups, such as carboxyl- or glycidyl-groups could enable covalent bonding between CNTs and hosting system, improving the interfacial stress transfer. Gojny et al. 2005 have investigated the effect of nanotube functionalization on the ultimate strength and fracture toughness of composite showing the mechanical performances at low nanotube content could be improved. A study of strengthen mechanism due chemical functionalization of the nanotubes is out of the scope of this work.

2.3 Modelling approaches

In spite of the outstanding mechanical properties of single tubes, long fibre reinforced nanopolymer composites exhibit a very limited improvement of mechanical performances, if compared to conventional advanced composites. This contradictory behaviour can be explained by considering that the reinforcing contribution of carbon nanotubes is yielded not only by their amount within the material, but also by the state of dispersion, orientation, shape and number of contacts within the hosting system. All these features play a critical role on the final reinforcement enhancement, and they should be taken into account to develop reliable models for prediction of nano-composite effective properties.

Since CNTs could be assimilated to “tiny” short particles, the classical micromechanics approaches for short fibre reinforced composites (SFRC) were employed as first attempts to develop predictive models of CNT/polymer composites (Coleman et al., 2006, Thostenson and Chou).

Voight and Reuss bounding models

A preliminary analysis to quantify the composite modulus can be performed by estimating the upper and the lower bounds. Bounding methods approximate both the stress and the strain field within the composite allowing the estimation of the modulus by a minimization of the overall strain energy. These methods cannot predict, directly, the composite stiffness, whereas they provide a proper range for the real composite stiffness.

The Voight and Reuss method represents the most simple bounding model. The lower and upper bounds are evaluated imposing, that fibre and reinforcement are subjected to the

same stress and strain field. The main assumption of this model concerns to the isotropic behaviour of the final composite system and, hence, when reinforcement and matrix have very different stiffness, the predicted bounds are quite far apart. As rule of thumb, the elastic modulus of the composite could be evaluated averaging the bounding values according to the following expression:

$$E_c = \lambda E_{up} + (1 - \lambda) E_{low} \quad (3)$$

The λ coefficient accounts for the reinforcement arrangement in the matrix, for random planar distribution it is assumed to be 3/8 (Tucker). The latter equation does not take into account any geometry of the fibre and it uses only three independent variables.

Halpin-Tsai model

A popular and widely adopted model to predict the stiffness of SFRC is the Halpin-Tsai equation (HT) that has been originally developed for continuous unidirectional composite (Halpin et al. 1976). This model is undoubtedly the most simple. The HT equations correlate empirically the property of composite material with specific characteristics of matrix and reinforcing phases together with their proportions and geometries. The model was derived by the work of Hermans, 1967 and Hill, 1964 by noting that three Hermans's equations for the stiffness could be re-written with a single expression according to the following equations:

$$E_{NC} = \left[\frac{3}{8} \frac{1 + \zeta \eta_L v_{NT}}{1 - \eta_L v_{NT}} + \frac{5}{8} \frac{1 + 2\eta_T v_{NT}}{1 - \eta_T v_{NT}} \right] \quad (4)$$

$$\eta_L = \frac{\left(\frac{E_{NT}}{E_m} \right) - 1}{\left(\frac{E_{NT}}{E_m} \right) + \zeta} \quad (5)$$

$$\eta_T = \frac{\left(\frac{E_{NT}}{E_m} \right) - 1}{\left(\frac{E_{NT}}{E_m} \right) + 2} \quad (6)$$

Halpin and Tsai, in adapting their approach to short-fibre composites, noted that the ζ parameter must lie between 0 and $+\infty$ and they suggested also that this parameter could be correlated with the geometry of the reinforcement. Moreover, when calculating the longitudinal Young modulus, it should vary as a function of the fibre aspect ratio (figure 8), whereas for the other engineering constants, an independency upon the reinforcement shape of the filler, could be suitably assumed.

The efficiency of the Halpin-Tsai equations has been valuably assessed for low concentration of filler. However it has been verified that at high volume fractions, discrepant predictions are computed. Modification of the HT model was published during the years mainly trying to correlate the ζ parameter with volume fraction. Despite the encouraging agreement of the data, the corrections are still based on fitting parameters without any theoretical supports (Nielsen et al., 1970, Lewis et al., 1970 and Hewitt et al., 1970)

Fig. 8. Reinforcement efficiency vs aspect ratio by H-T model

Thostenson and Chou approach of H-T models

Assuming the Halpin-Tsai model, Thostenson and Chou considered that, in the case of MWCNT, only the outer shell would carry the load as logical assumption of the relatively low bonding with inner layers. According to this assumption, the effective MWCNT elastic modulus was evaluated by considering the application of all loads only to the outer cross section, according to the following equation:

$$E_{eff} = \frac{4t}{d} E_{NT} \tag{7}$$

where *t* and *d* represent, respectively, the graphite layer thickness (0.34 nm), and, the nanotube outer diameter; while the ζ parameter, for low volume fractions, is assumed as:

$$\zeta = 2 \frac{l}{d} \tag{8}$$

The authors have added to the simple aspect ratio, the nanotube diameter as reasonable parameter influencing the reinforcement efficiency. The following equation reports the longitudinal elastic modulus as function of fibre aspect ratio and fibre diameter:

$$E_L = E_m \frac{\left(1 + 2 \left(\frac{l}{d} \right) \left(\frac{\left(\frac{E_{NT}}{E_m} \right) - \left(\frac{d}{4t} \right)}{\left(\frac{E_{NT}}{E_m} \right) - \left(\frac{l}{2t} \right)} \right) v_{NT} \right)}{\left(1 - \left(\frac{\left(\frac{E_{NT}}{E_m} \right) - \left(\frac{d}{4t} \right)}{\left(\frac{E_{NT}}{E_m} \right) - \left(\frac{l}{2t} \right)} \right) v_{NT} \right)} \tag{9}$$

Predictions computed by using Thostenson correction show a reduced level of efficiency at constant aspect ratio for each curve (figure 9) but trends substantially similar to the Halpin-Tsai predictive curves. Shokrieh and Rafiee, 2010 have demonstrated through FE analysis that Halpin-Tsai based methods overestimates the composite modulus and they have suggested to adjust the model predictions by introducing an equivalent solid reinforcement with interphase region as filler.

Fig. 9. Reinforcement efficiency prediction according to H-T/Thostenson modifications for different aspect ratios, AR=5, 10, 50, 100, 500

Yeh correction of H-T equation

Methods based on the previous correction for the H-T approach have revealed a good agreement with experimental data only in the dilute regime whilst they are unable to predict the non-linear behaviour observed by many authors at higher filler content (Yeh et al., 2006; Martone et al., 2010). Further modifications were introduced by Yeh et al., 2006 in order to account for the aggregation effect of carbon nanotube on mechanical response of the final nano-composite. They suggested to modify the shape factor ζ by adding an exponential term to model the possible nanotube aggregation, according to the following equation:

$$\zeta = 2 \frac{1}{d} e^{-(a v_{NT} + b)} \quad (10)$$

where a and b represent adjustable parameters.

Higher levels of aggregation and networking of CNT within the final system necessarily suggest an higher aggregation-associated values (a and b).

Although this correction leads up to a good correlation with experimental data, this approach is rather sophisticated since it needs the earlier determination of three constants (a, b and c). Moreover the physical meaning of the two aggregation factors is missed.

Fig. 10. Reinforcement efficiency prediction according to H-T/ Yeh correction for different aspect ratios, AR=5, 10, 50, 100, 500

Figure 10 reports the predictive curves of reinforcement efficiency as function of nanofillers volume content for different aspect ratio.

Shear Lag based approach

Among the different methods based on the mixtures rule, the approach based on “*Shear Lag*” theory indeed represents the most common, intuitive and reliable. In fact, despite some serious speculative flaws, this model probably has gained popularity, due to the lack of algebraic complexity and the physical appeal of the original scheme. The main limitation of this model is represented by the capability to predict only longitudinal stiffness of the system.

Cox’s model

Cox (1952) introduced the concept of the effective tensile modulus of a short fibre embedded into a matrix by defining the efficiency, η , as the reduction ratio of its intrinsic tensile modulus, E_f . This approach, in the case of aligned fibres, is described by the following equations:

$$E = \eta_l v_f E_f + (1 - v_f) E_m \tag{11}$$

$$\eta_l = 1 - \frac{\tanh\left(a \frac{l}{d}\right)}{\left(a \frac{l}{d}\right)} \tag{12}$$

where η_l is the length efficiency factor and the parameter a , accounts for the fibre packing and the Young moduli ratio. Developments of the Cox model were conducted mainly upon

the way of choosing suitably the radius of the surrounding matrix cylinder (hexagonal, circular, square etc.).

Readers interested in short fibre modelling approach for the case of unidirectional composite are remanded to an awesome overview by Tucker et Liang, 1999.

Although the mentioned models were developed for micro-sized reinforcing elements and for considerable volume content rather than nano-metric structures and dilute regime, many researchers have attempted to model CNTs reinforcement effect by using these approaches. Results are not encouraging, unless some different issues, related mainly with the nano-metric structure of these unconventional fillers are accounted for.

The direct implementation of the reported models to the case of nano-composites reveals critical discrepancy and inefficiency due to the main assumption that only the specific content of CNTs drives the reinforcement efficiency. Actually, conventional modelling approaches for short or particulate composites neglect issues such as, topology, dispersion morphology, contacts among the nano-fillers and possible sticky potential which indeed represent critical features in the case of nano-filler for predictive models.

The topological configuration of the fillers, as example, has been demonstrated to significantly act in the case of the electrical conductivity of the final nano-composite. In fact, according to the available literature, it is well known, that percolative phenomenon drives the conductive-non conductive behaviour of nano-composites (Gojny et al., 2005, Kovacs et al., 2007, 2009).

Despite conductive properties of nano-composites have been well-described in the framework of percolation theory and an appreciable agreement with a huge amount of experimental data is reported, a lack of theoretical understanding and modelling capability for mechanical behaviour is still missing.

In the last decade, many researchers and scientists have proposed analytical and numerical models to predict the mechanical behaviour of polymer matrix filled with carbon nanotubes. Most of the works were essentially based on modification of classical approaches originally developed for short fibre and particulate composites, by considering, in some cases, specific features such as waviness or topological distribution of nano-fillers.

Carman-Reifsnider correction

Among the different variants of the rule of mixtures, the most prominent model has been developed by Carman-Reifsnider, 1992. Assuming a coaxial fibre-matrix scheme, i.e. cylindrical fibres surrounded by a concentric matrix shell, the fibre volume fraction results a square function of the radii ratio, thereby the stress transfer coefficient becomes:

$$a = \sqrt{\frac{-3E_m}{2E_{NT} \ln(v_{NT})}} \quad (13)$$

The length efficiency factor (η_l) approaches to 1 as the aspect ratio increases, highlighting that higher aspect ratio fillers are preferred to improve the matrix stiffness at low reinforcement content. The main advantages of this model concerns with the possibility to overcome the non-linear behaviour (figure 11) reported by experimental data expressing the reinforcement efficiency as follows:

$$\frac{E_c - E_m}{E_m} = \left(\eta_l \frac{E_{NT}}{E_m} - 1 \right) v_{NT} \quad (14)$$

Fig. 11. Cox’s model prediction of reinforcement efficiency according Carman-Reifsnider correction for different aspect ratios, AR=5, 10, 50, 100, 500

Fig. 12. Reinforcement efficiency predictions according to shear-lag approach including Nairn correction for different aspect ratios, AR=5, 10, 50, 100, 500

Energy-based model by Nairn

A severe flaw of the shear lag based approach is the prediction of composite stiffness at very low fibre volume fraction. Nairn, 1997 published an accurate study on the use of shear lag method. In this work a modified definition of the stress transfer parameter, based on energy concerns, is proposed. Equations 15 and 16 report the expression of shear-lag based model with Nairn modifications to evaluate the composite modulus

$$\beta = \sqrt{\frac{2}{E_f E_m} \cdot \frac{E_f V_f + E_m (1 - V_f)}{(1 - V_f)}} + \frac{1}{\left(4 \cdot \frac{E_f}{2(1 + \nu_f)}\right) + \left(2 \cdot \frac{E_m}{(1 + \nu_m)} \cdot \left(\frac{1}{1 - V_f} \ln\left(\frac{1}{V_f}\right) - 1 - \frac{1 - V_f}{2}\right)\right)} \quad (15)$$

$$E_c = \frac{V_f E_f + (1 - V_f) E_m}{1 + \frac{E_f}{E_m} \frac{V_f}{1 - V_f} \frac{\tanh(\beta \ell/2)}{\beta \ell/2}} \quad (16)$$

The predictions computed by the Nairn suggested shear lag model are reported in figure 12 for different aspect ratio values up to 10% percentage of filler volume fraction.

Shear-lag modification by Omid et al.

The relationship between mechanical properties of the final nano-composite system and CNT loading could be assumed linear only at low volume fraction. Omid et al., 2010 have suggested a modified version of eq. 11 by adding an exponential factor as reported in eq. 11:

$$\frac{E_c - E_m}{E_m} = \left(\eta \frac{E_{NT}}{E_m} - 1 \right) v_{NT} e^{\alpha v_{NT}} \quad (17)$$

Even though the fitting is much more congruent with experimental data, the exponential factor is not correlated with any physical justification or theoretical assumption weakening the final modelling validity. A further modification to include nanotube waviness and spatial orientation distribution, is reported in eq. 18, according to the following expression:

$$\eta = \eta_0 \eta_t \eta_w \quad (18)$$

The distribution of oriented nanotubes, included in the model by the η_0 factor, results 1/3 and 1/5 for randomly oriented CNT, in 2D (in plane) and in 3D respectively. The α coefficient in equation (17) is defined as:

$$\alpha = \frac{\ln \beta}{v_{NT}}, \quad \beta = \frac{\left(\frac{E_c - E_m}{E_m} \right)}{\left(\eta \frac{E_{NT}}{E_m} - 1 \right) v_{NT}} \quad (19)$$

The above method provides good predictions of CNT-Polymer composite mechanical behaviour. However, it needs as input not only the experimental parameter, α , obtained by

Fig. 13. Reinforcement efficiency predictions for shear lag model according to Cox-Carman-Reifsneider-Omid corrections for different aspect ratios, AR=5, 10, 50, 100, 500

testing the nanocomposite at the high CNT volume fraction, but also the fitting parameter, η_w , associated with CNT waviness (figure 13).

Attempts have been proposed to account for the suspension of cluster within the material (Guzma'n de Villoria et al., 2007, Chatterjee, 2008). To the best author knowledge, a proper developed theory able to take into account nano-composite topology is still missed. Moreover, all the above modifications were proposed as rule of thumb to predict the elastic behaviour of such composites through the introduction of empirical correction factors characterised by weak physical meaning.

All analysed models report as main assumption the uniform dispersion of the filler content. Indeed, this hypotheses seems not realistic to represent CNT-Polymer systems, as widely demonstrated by the available literature. Dispersion technique, processing parameters and typology of the hosting matrix will modify the final nano-composite, strongly affecting its final mechanical performances. Contacts among nanotubes can be assumed to occur with a major probability in the case of higher nano-filler content. Moreover, the assumption of interconnected nanostructure leads to the consideration that excluded volume and effective aspect ratio of nano-reinforcements differ significantly from the nominal value.

In the following paragraph, the rule of mixture will be introduced highlighting a recent modification of the original model to account for the nanotubes connectivity published by Martone et al., 2011. Recent experimental data will be also analysed and compared with model predictions to support the validity and the effectiveness of this approach.

3. Recent advanced in CNT reinforcement effect

3.1 Tube contact effects in the Cox's model

To the best knowledge of the authors, all the proposed methods to predict mechanical performances of nano-composites are essentially based on semi-empirical modification of short fibre micromechanics. The available models do not account for the progressive formation and growth of connected paths among loaded nano-elements, which may represent the most relevant features for the enhancement effect of mechanical property. The main models (Halpin-Tsai and Shear-lag) presented in the previous paragraph and various modifications (Cox, Nairn, Reifsnider, Yeh) show a negligible dependency of the reinforcement efficiency on the nano-filler aspect ratio. The only approach, which considers a strong relation between the efficiency and the aspect ratio, is shown by the Omid et al. correction, which in turn, requires experimental data at very high CNT content and a curve fitting parameter as input for the computation of the model. The connectedness and the waviness of the nanofiller within the hosting matrix indeed affect the mechanical enhancement of the final nano-composite. For this reason, a predictive model for the mechanical reinforcement efficiency of CNT should take necessarily into account such features.

In this paragraph an attempt to include the connectedness of tubes and the waviness feature of the carbon nanotubes within the hosting medium is discussed and described. The main achieved results, experienced on CNT/nano-composites by many researchers, could be correctly summarised as follows:

1. the dependence of the effective reinforcement modulus upon the tubes aspect ratio. In the very dilute regime the effective elastic modulus of CNT depends directly on the averaged aspect ratio of the filler.
2. the reduction of mechanical efficiency at increasing volume content. As the nanotube content increases due to the progressive increment of tube-to-tube contacts the effectiveness of transferring load decreases.

Shear-lag-based approaches have been widely used to analyse the effect of the aspect ratio on mechanical of carbon nanotubes composite. The main assumption of these models is the perfect adhesion between the phases where the stress transfer occurs via a shear mechanism. By applying the shear lag models, the composite modulus results an average value of the specific components modulus that are reduced by a numerical factor depending on the aspect ratio of the reinforcing filler. In this case, the most prominent expression for the prediction of the nano-composite Young's modulus is given by equation 20:

$$\begin{aligned}
 E_c &= E_\eta \cdot \phi + E_m \cdot (1 - \phi) \\
 E_\eta &= \eta \cdot E_{NT} \\
 \eta &= 1 - \frac{\tanh(K \cdot AR)}{(K \cdot AR)} \\
 K &= \sqrt{\frac{-\frac{2}{1+\nu_m}}{\frac{E_{NT}}{E_m} \cdot \ln(\phi)}}
 \end{aligned} \tag{20}$$

The stress transfer parameter, K , is computed, according to the Carman-Reifsnider assumption, considering, as fibres arrangement, a cylindrical packing surrounded by the

matrix. While the progressive formation of contacts among tubes creates a fully connected web which improves the materials conductive (thermal and electrical) behaviour, the mechanical performances are characterized by an opposite tendency. Actually, contacts among the “tubes” create points at which negligible load transfer could be assumed. Therefore, a predictive model for such nano-composites needs to account for arising number of contact points with the CNT content. With the aim to achieve this latter target, the study of particle packing is paramount; nevertheless, study of the density of random rods or fibre packing has not received great attention until the work published by Philipse in 1996, on the stacking configuration of high aspect ratio rods.

The Random Contact Model is based on the assumption that two particles of any shape can contact with a probability which is averagely independent on other contact formations, in other terms, if contacts are uncorrelated, their number for each particle varies linearly with the particle concentration. The theory states that the average number of contacts per particle $\langle c \rangle$ is dependent on the normalized average excluded volume, V_{ex} , and the particles volume fraction, ϕ , according to the following expression:

$$\langle c \rangle = \phi \cdot \frac{V_{ex}}{V_p} \quad (21)$$

where V_p is the particle volume.

The excluded volume of an object is defined as the volume around an object into which the centre of another similar object is not allowed to enter if overlapping of the two objects is to be avoided. According to Onsager, 1949, the average excluded volume of a pair of random rods, modelled by cylinders of length L with two hemispherical caps of diameter D , is given by

$$V_{ex} = \frac{\pi}{2} \cdot L^2 D + 2\pi \cdot D^2 L + \frac{4}{3} \pi \cdot D^3 \quad (22)$$

A further feature to account for the correct computation of the excluded volume of “tube” elements, is related to the achieved waviness in the final nano-composite system. Waved objects, in fact, will necessarily induce a further contribution to the excluded volume.

Thus the average number of contacts per particle $\langle c \rangle$ for tubes is dependent on “tube” aspect ratio (AR) and their final waviness level (w), according to the following expression:

$$\langle c \rangle = w \cdot \phi \cdot \left(4 + \frac{3AR^2}{3AR + 2} \right) \quad (23)$$

where the w represents the “tube” waviness level. This parameter has been introduced as the ratio between the effective average excluded volume and that evaluated for a straight rod to account for the CNT waved arrangement within the final nano-composite.

A number of theoretical studies are available in literature to evaluate the effect of nanotube waviness on the excluded volume. An exhaustive discussion on the calculation of excluded volume for curved rods is beyond the scope of this work. Remarkable efforts have been reported by Behran and Sastry, 2007, Li and Chou, 2007, Ma and Gao, 2008, nevertheless, these studies are limited by the main assumption of rod shapes. As stated previously, contacts between nanotubes imply a reduction of the stress transfer efficiency of the reinforcement, afterwards the rule of mixtures could be modified by reducing the stress transfer coefficient by the average number of contacts

$$\eta = 1 - \frac{\tanh\left(\frac{K \cdot AR}{1 + \langle c \rangle}\right)}{\left(\frac{K \cdot AR}{1 + \langle c \rangle}\right)} \tag{24}$$

Below the hypotheses of contacting nanotubes, the effective aspect ratio of filler could be defined as

$$AR_e = \frac{AR}{1 + \langle c \rangle} \tag{25}$$

Figure 14 and 15 report the predictive curves of the present contact tube model based on rule of mixture in the case of straight and waved tubes respectively over almost four filler volume fraction percentage decades.

In particular, predictions have been computed considering (fig.14) a constant waviness level ($w=1$) and, hence, schematizing the “tube” elements as rigid (i.e. neglected contribution of the excluded volume associated to the waviness level) for different average aspect ratio, $AR=5, 10, 50, 100, 500$. It is worth to observe that the original shear lag approach is not able to describe the progressive reduction of reinforcement efficiency, whilst modified expression including random contact model, excluded volume and waviness may very accurately reproduce the experimental values at very dilute regime. Waviness accounts the augmentation of contacts between nanotubes due to the curliness of fillers.

Fig. 14. Predictions of reinforcement efficiency for “straight tubes” ($w=1$) at different aspect ratio $AR= 5, 10, 50, 100, 500$ according to the developed model

Fig. 15. Predictions of reinforcement efficiency according to the developed models for the case of AR=50 at different magnitudes of waviness, $w=0,1,2,5$

3.2 Comparison: literature data vs modified Cox’s model

In this section, the proposed modification of Cox’s model presented in paragraph 3.1, will be applied to available literature experimental data. Topological parameters (AR_e and w) will be evaluated by curve fitting for each set of data.

Table 1 reports the details of the considered CNT nano-composite taken from the scientific literature of the last 10 years. It can be noticed that the data set are related to different typology of carbon nanotubes and hosting matrix. The aspect ratio is spread over three decades and, moreover, experimental results are associated to nano-composite samples that have been manufactured by different techniques: high energy mixing such as sonication or low or moderate mixing such as mechanical stirring by magnetical agitation.

Figures 16 a) and b) show the modelling curves and corresponding experimental data sets. Model parameters are the CNTs elastic modulus, kept constant at the value of 3 TPa for all simulations, CNT aspect ratio, and the CNT waviness parameter, evaluated by curve fitting.

In figure 16, for each data set the fitting parameters are overlaid. It is worth to note that the waviness parameter could be correlated to the aspect ratio, namely the higher the aspect ratio the higher the waviness parameter. Table 2 reports the best fitting parameters of the presented model, evaluating the effective filler aspect ratio, AR_e , and waviness parameter, w for each set of data. It is important to notice that the fitting aspect ratio falls in the nominal range for nanocomposites mixed by ultrasonication, whilst nanocomposites mixed by mechanical stirring led to an effective aspect ratio lower than the nominal one.

Reference	Matrix	MWNT	Manufacturing	Diameter [nm]	AR	E _η [Gpa]
<i>Omidi et al., 2010</i>	Epoxy LY-5052	RIPI CVD	Sonication	10-50	20-300	148
<i>Ogasawara et al., 2004</i>	Polyimide Tri-A-Pi	CNRI CVD	Mechanical Stirring	20-100	10-200	13
<i>Martone et al. 2010</i>	Epoxy RTM6	CVD	Sonication	9.5	20-1000	1784
<i>Martone et al. 2011</i>	Epoxy RTM6	CVD	Sonication	110-170	22-52	144
<i>Martone et al. 2011</i>	Epoxy RTM6	CVD	Sonication	40-70	7-50	71
<i>Xiao et al., 2007</i>	Polyethylene LDPE	NanoLab CVD	Mechanical Stirring	10-20	50-500	6
<i>Yeh et al., 2006</i>	Phenolic PF-650	Own CVD	Sonication	15-40	50-300	221
<i>Ayhatollai et al. 2011</i>	Epoxy ML-506	CVD	Stirring + Sonication	10-30	250-1000	184
<i>Liu et al. 2004</i>	Nylon6	CVD	Melt Compounding	7-20	500-2000	472
<i>Kanagaraj et al., 2007</i>	Polyethylene HDPE	Nanotech CVD	Magnetical Stirring	60-100	50-250	68

Table 1. Physical properties of nanocomposites considered from available experimental data.

a)

Fig. 16. Comparison between experimental data and model predictions. The fitting parameters are superimposed to each curve.

	AR	w
<i>Onidi et al., 2010</i>	20	1.2
<i>Ogasawara et al., 2004</i>	4.5	0.3
<i>Martone et al. 2011 AR505</i>	1000	18.0
<i>Martone et al. 2011 AR30</i>	42	11
<i>Martone et al. 2011 AR55</i>	28	4.4
<i>Xiao et al., 2007</i>	11	0.65
<i>Yeh et al., 2006</i>	28	2.0
<i>Ayhatollai et al. 2011</i>	28	1.6
<i>Liu et al. 2004</i>	75	1.41
<i>Kanagaraj et al., 2007</i>	29	2.6

Table 2. Fitting parameters (AR-aspect ratio and w-waviness) for different data sets.

4. Conclusion

The potential usage of carbon nanotubes to enhance the mechanical behaviour of matrix polymer indeed represents a potential breakthrough for a new generation of advanced polymer composites. The mechanical reinforcement of a polymer by carbon nanotubes is highly attracting the effort of the scientific community mainly for two reasons. Firstly, the wide amount of available experimental data in the scientific literature results controversial

and uncertainties arise regarding the effects induced by the different carbon nanotubes geometry, loading fraction, network formation and processing conditions.

Secondly, reliable models, for the prediction of the reinforcement feature with increasing filler content, are still not available as currently used models do not correctly represent the various issues associated with content, morphology and type of nano-fillers. Some of these issues have been considered in the proposed reinforcement efficiency model which the chapter presents and describes. Experimental findings support the evidence that in carbon nanotube reinforced polymers, contacting “tube” fillers implies a significant decrease of stress transfer efficiency between reinforcing nanotubes and hosting matrix via a reduction of the effective filler length. Philipse’s model of random contacting nanotubes has been considered to allow the evaluation of the average reduction of the effective tube aspect ratio by means of reinforcing particle excluded volume computation. Finally, the shear lag theory of the short fibre micromechanics provides the necessary framework for the evaluation of the composite modulus. The nanotubes aspect ratio stands as the controlling parameter for the determination of the mechanical properties of CNTs reinforced polymers. A physical parameter accounting for the waviness of the nanotubes within the polymer matrix is provided in order to describe the deviation of the excluded volume evaluated for curved nanotubes from the straight rod assumption. The model is able to reproduce the non linear reinforcement behaviours of different aspect ratios carbon nanotubes in different matrices reported in the literature. A topological explanation of the reduction of the reinforcement efficiency of carbon nanotubes within polymer matrices upon their contacting and clustering has been provided addressing the major phenomenological behaviours. Further investigation is needed to better clarify the role of nanotubes curvature within a hosting polymer matrices on elastic modulus of the final nano-composite system.

5. References

- Ayatollahi, M.R.; Shadlou, S.; Shokrieh, M.M. (2011). Fracture toughness of epoxy/multi-walled carbon nanotube nano-composites under bending and shear loading conditions. *Materials and Design*, Vol. 32, pp.2115–2124. doi:10.1016/j.matdes.2010.11.034.
- Behran, L.; Sastry, A. M. (2007). Modeling percolation in high aspect-ratio fibre systems. II. The effect of waviness on the percolation onset. *Physical Review E*, Vol. 75, N.041121.
- Carman, G.P.; Reifsnider K.L. (1992). Micromechanics of short-fibre composites. *Composites Science and Technology*, Vol. 43, N. 2, pp. 137-146.
- Chatterjee, A.P. (2008). Modeling the elastic moduli of fibre networks and nanocomposites: Transversely isotropic filler particles. *Journal of Applied Physics*, Vol. 103, pp. 064316.
- Coleman, J.N.; Khan, U.; Blau, W.J.; Gun’ko, Y.K. (2006). Small but strong: A review of the mechanical properties of carbon nanotube-based composites. *Carbon*, Vol. 44, pp. 1624-1652. doi: 10.106/j.carbon.02.038.
- Cox, H.L. (1952). The elasticity and strength of paper and other fibrous materials. *British Journal of Applied Physics*, Vol. 3, N. 3, pp. 72-76. doi: 10.1088/0508-3443/3/3/302.
- De Zhang, W.; Shen, L.; Phang, I.Y.; Liu T.X. (2004). Carbon nanotubes reinforced nylon-6 composite prepared by simple melt-compounding. *Macromolecules*, Vol. 37, N. 2, pp. 256–259.

- Gojny, F.H.; Wichmann, M.H.G.; Fiedler, B.; Schulte, K. (2005). Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites – A comparative study. *Composites Science and Technology*, Vol. 65, pp.2300–2313.
- Guzma'n de Villoria, R.; Miravete, A. (2007). Mechanical model to evaluate the effect of the dispersion in nanocomposites. *Acta Materialia*, Vol. 55, pp. 3025–3031.
- Halpin J. C. Kardos J. L. (1976) The Halpin±Tsai Equations: A Review. *Polym Eng Sci*, Vol. 16, pp. 344-352.
- Hermans, J.J. (1967) The elastic properties of fiber reinforced materials when the fibers are aligned. *Proc. Kon Ned Akad v Wetensch B*, Vol. 65, pp. 1-9
- Hewitt RL, de Malherbe MC. (1970) An Approximation for the Longitudinal Shear Modulus of Continuous Fibre Composites. *Journal of Composite Materials*, Vol. 4, pp. 280-282.
- Hill, R. (1964) Theory of Mechanical Properties of Fibre-Strengthened Materials: I Elastic Behaviour. *Journal of Mechanical Physics of Solids* Vol. 12, pp. 199-212.
- Hussain, F.; Hojjati,M.; Okamoto, M.; Gorga, R.E. (2006). Review article: Polymer-matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview. *Journal of Composite Materials*, Vol. 40, N. 17, pp. 1511-1575.
- Kanagaraj, S.; Varanda, F.R.; Zhiltsova, T.V.; Oliveira, M.S.A.; Simoes, J.A.O. (2007). Mechanical properties of high density polyethylene/carbon nanotube composites. *Composites Science and Technology*, Vol. 67, pp. 3071–3077.
- Kovacs, J.Z.; Mandjarov, R.E.; Blisnjuk, T.; Prehn, K.; Sussiek, M.; Müller, J.; Schulte, K.; Bauhofer, W. (2009). On the influence of nanotube properties, processing conditions and shear forces on the electrical conductivity of carbon nanotube epoxy composites. *Nanotechnology*, Vol. 20.
- Kovacs, J.Z.; Velagala, B.S. ; Schulte, K.; Bauhofer W. (2007). Two percolation thresholds in carbon nanotube epoxy composites. *Composite Science and Technology*, Vol. 67, pp. 922-926.
- Lewis TB, Nielsen LE. (1970) Dynamic Mechanical Properties of Particulate-Filled Composites. *Journal of Applied Polymer Science* Vol. 14, pp. 1449-1471.
- Li, C.; Chou, T.W. (2004). Modeling of elastic buckling of carbon nanotubes by molecular structural mechanics approach. *Mechanics of Materials*, Vol. 36, pp.1047–1050.
- Li, C.; Chou, T.W. (2007). Continuum percolation of nanocomposites with fillers of arbitrary shapes. *Applied Physics Letters*, Vol. 90, N.174108.
- Liu, T.X.; Phang, I.Y.; Shen, L.; Chow, S.Y.; Zhang, W. D. (2004). Morphology and mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites. *Macromolecules*, Vol. 37, N. 19, pp. 7214–7222.
- Ma, P.C.; Kim, J-K; Tang, B.Z. (2007). Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites. *Composites Science and Technology*, Vol. 67, pp. 2965–2972.
- Ma,H.M.; Gao X.L. (2008). A three-dimensional Monte Carlo model for electrically conductive polymer matrix composites filled with curved fibres. *Polymer*, Vol. 49, pp. 4230–4238. doi:10.1016/j.polymer.2008.07.034.
- Martone, A.; Faiella, G.; Antonucci, V.; Giordano, M.; Zarrelli, M. (2011). The effect of the aspect ratio of carbon nanotubes on their effective reinforcement modulus in an epoxy matrix. *Composites Science and Technology*, doi: 10.1016/j.compscitech.2011.04.002.
- Martone, A.; Formicola, C.; Giordano, M.; Zarrelli, M. (2010). Reinforcement efficiency of multi-walled carbon nanotube/epoxy nano composites. *Composites Science and Technology*, Vol. 70, Issue 7, pp. 1154-1160, doi:10.1016/j.compscitech.2010.03.001.

- Nairn, J.A. (1997). On the use of shear-lag methods for analysis of stress transfer in unidirectional composites. *Mechanics of Materials*, Vol. 26, pp. 66-80.
- Nielsen LE. 1970. Generalized Equation for the Elastic Moduli of Composite Materials. *J Appl Phys*, vol. 41, pp. 4626-4627.
- Ogasawaraa, T.; Ishidaa, Y.; Ishikawaa, T.; Yokota, R. (2004). Characterization of multi-walled carbon nanotube/phenylethynyl terminated polyimide composites. *Composites: Part A*, Vol. 35, pp. 67-74.
- Omidi, M.; Hossein Rokni, D. T.; Milani, A.S.; Seethaler R.J.; Arasteh, R. (2010). Prediction of the mechanical characteristics of multi-walled carbon nanotube/epoxy composites using a new form of the rule of mixtures. *Carbon*, Vol. 48, pp. 3218-3222. doi:10.1016/j.carbon.2010.05.007.
- Onsager, L. (1949). The effects of shape on interaction of colloidal particles. *Annals of the New York Academy of Science*, Vol. 51, pp. 627-659.
- Philipse, A.P. (1996). The Random Contact Equation and Its Implications for (colloidal) Rods in Packings, Suspensions, and Anisotropic Powders. *ACS publications Langmuir*, Vol. 12, N. 5, pp. 1127-1133.
- Shaffler, M.S.P and A.H.Windle, (1999) Fabrication and characterization of carbon Nanotube/Poly(vinyl alcohol) Composites. *Advanced Materials*, Vol.11, N.11, pp. 937-941.
- Shokrieh, M.M.; Rafiee, R. (2010). Investigation of nanotube length effect on the reinforcement efficiency in carbon nanotube based composites. *Composite Structures*, Vol. 92, pp. 2415-2420. doi:10.1016/j.compstruct.2010.02.018.
- Sun, L.; Warren, G.L.; O'Reilly, J.Y.; Everett, W.N.; Lee, S.M.; Davis, D. et al. (2008). Mechanical properties of surface-functionalized SWCNT/epoxy composites. *Carbon*, Vol. 46, pp. 320-328.
- Thostenson, E.T.; Chou, T.W. (2003). On the elastic properties of carbon nanotube-based composites: modeling and characterization. *Journal of Physics D: Applied Physics*, Vol. 36, pp. 573-582.
- Thostenson, E.T.; Chou, T.W. (2006). Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites. *Carbon*, Vol. 44, pp. 3022-3029.
- Treacy, M.M.J.; Ebbesen, T.W.; Gibson, J.M. (1996). Exceptional high Young's modulus observed for individual carbon nanotubes. *Nature*, Vol. 381, pp.678-680.
- Tucker III, C.L.; Liang, E. (1999). Stiffness predictions for unidirectional short-fibre composites: Review and evaluation. *Composite Science and Technology*, Vol. 59, pp. 655-671.
- Valavala, P.K.; Odegard, G.M. (2005). Modeling techniques for determination of mechanical properties of polymer composites. *Reviews on Advanced Material Science*, Vol. 9, N. 1, pp. 34-44.
- Wang, Q.; Duan, W. H.; Liew, K. M.; He, X. Q. (2007). Inelastic buckling of carbon nanotubes. *Applied Physics Letters*, Vol. 90, pp. 033110.
- Xiao, K.Q.; Zhang, L.C., Zarudi, I. (2007). Mechanical and rheological properties of carbon nanotube-reinforced polyethylene composites. *Composites Science and Technology* Vol. 67, pp. 177-182.
- Yeh, M.K.; Tai, N.H.; Liu, J.H. (2006). Mechanical behavior of phenolic-based composite materials. *Carbon*, Vol. 44, pp. 1-9. doi:10.1016/j.carbon.2005.07.005.
- Zhou, Y.; Pervin, F.; Lewis, L.; Jeelani, S. (2008). Fabrication and characterization of carbon/epoxy composites mixed with multi-walled carbon nanotubes. *Material Science and Engineering A*, Vol. 475, pp. 157-65.

Carbon Nanotubes - From Research to Applications

Edited by Dr. Stefano Bianco

ISBN 978-953-307-500-6

Hard cover, 358 pages

Publisher InTech

Published online 20, July, 2011

Published in print edition July, 2011

Since their discovery in 1991, carbon nanotubes have been considered as one of the most promising materials for a wide range of applications, in virtue of their outstanding properties. During the last two decades, both single-walled and multi-walled CNTs probably represented the hottest research topic concerning materials science, equally from a fundamental and from an applicative point of view. There is a prevailing opinion among the research community that CNTs are now ready for application in everyday world. This book provides an (obviously not exhaustive) overview on some of the amazing possible applications of CNT-based materials in the near future.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Alfonso Martone, Gabriella Faiella, Vincenza Antonucci, Michele Giordano and Mauro Zarrelli (2011). Investigation of the Effective Reinforcement Modulus of Carbon Nanotubes in an Epoxy Matrix, Carbon Nanotubes - From Research to Applications, Dr. Stefano Bianco (Ed.), ISBN: 978-953-307-500-6, InTech, Available from: <http://www.intechopen.com/books/carbon-nanotubes-from-research-to-applications/investigation-of-the-effective-reinforcement-modulus-of-carbon-nanotubes-in-an-epoxy-matrix>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](https://creativecommons.org/licenses/by-nc-sa/3.0/), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen